

**REMARKS**

Claims 20-22, 24-31, and 33-39 are pending in the application.

**Claim Rejections - 35 U.S.C. 112**

Claims 20, 25, 31 stand rejected under 35 U.S.C. 112, 2nd paragraph, as being indefinite.

In claim 20, the examiner objects to "minimally reduced", "bi-continuous", and "hydrolysis component on PVAc basis".

Native starch has commonly a molecular weight of  $25-60 \times 10^6$  g/mol, i.e., a molecular weight that is extremely high. This wide range is the result of natural fluctuations and measuring imprecisions when determining such high molecular weights. The invention provides as an example a molecular weight of  $40 \times 10^6$  g/mol for the average molecular weight of native potato starch (see table bridging pages 6 and 7).

The molecular weight of starch is drastically reduced by thermoplastic processing of any kind, for example, by the effect of shearing forces, heat, and chemical decomposition.

The molecular weight (MW) of native starch when being processed to thermoplastic starch (TPS) is reduced; this can also be seen in the aforementioned table. Example No. 1 shows that the MW of TPS is reduced to  $13.2 \times 10^6$  g/mol (page 7, line 1, of the instant application) in comparison to native starch. It is also shown that commercially available products such as MaterBi have MW reduced by a factor 100 relative to native starch.

In the polymer blend according to the invention, the molecular weight of the starch is however only minimally reduced. The table on page 7 of the instant application shows that the addition of the catalyst (dilute  $\text{HNO}_3$ ) alone reduces the molecular weight of the starch significantly (molecular weight  $1.4$  to  $4 \times 10^6$  g/mol) and that the inventive addition of the hydrolysis component of PVAc (samples No. 4 through 6) counteracts the starch decomposition caused by acid. The addition of PVAc hydrolysis component according to the invention even has the effect that the starch has a higher molecular weight than that of known thermoplastic starch (example No. 1). In comparison to native starch (example No. 7, MW  $40 \times 10^6$  g/mol), the molecular weight is lowered by less than 50 % (examples Nos. 4 through 6: 24 to 25 %) when adding the PVAc hydrolysis component according to

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the invention. Accordingly, the starch processing according to the present invention leads to minimally reduced molecular weights. In applicant's opinion, the specification provides sufficient disclosure for the term minimally reduced.

As a result of the high molecular weight of the starch in the polymer blend according to the invention, the mechanical properties are improved (stress at break, stretch at break, and the modulus of elasticity). Because of the higher molecular weight of the starch in the polymer blend according to the invention, the starch ratio can be increased without compromising the mechanical properties. Because of the higher starch content, the total energy consumption for producing the blend and the manufacturing costs for producing the blend are lowered while the blend exhibits improved biological decomposition. This is in line with the economical and ecological goals of the present invention.

As regards the term bi-continuous phase structure, applicant submits two publications. Bi-continuous phase structure refers to a two-phase structure. The first publication, "Formation of Co-Continuous Open-Celled Morphologies in Biopolymers", by Todd Crosby and Sachin Velankar of the Chemical and Petroleum Department of the University of Pittsburgh, discloses that the terms co-continuous and bi-continuous are synonyms (see line 2 of the first paragraph of publication) and that "in such bi-continuous or co-continuous blends each phase is interlocked within one another and removal of one phase will leave the other self-supporting".

Also, the attached article from the Journal of Macromolecular Science (Vol. C43, No. 1, pp. 87) by Petra Pötsch and D.R. Paul discloses that:

*"In a co-continuous polymer blend each component is a polymer phase with its own internal network-like structures from which its properties result. This general definition includes different scales of mixing. In fact, in the literature, co-continuous phase structures are often described as interpenetrating polymer networks (IPNs), .... The term IPN more typically refers to a bi-continuous structure on the mixing level of polymer chains... In a binary co-continuous blend the surface of each phase is an exact topological replica of the other; light are complementary reversed (antitropic) as shown in Fig. 2 (page 90 to 92)."*

Therefore, the term bi-continuous is well known in the art; any person skilled in the

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art will be aware of its meaning.

This definition is consistent with the instant specification where the properties of the bi-continuous phase morphology are disclosed on page 5, third paragraph.

*"The bi-continuous phase structure has also the advantage that the hydrophobic properties of the synthetic polymer component even for a relatively minimal proportion within the total mixture are imparted to the material as a whole. At the same time, the properties of the thermoplastic starch, such as high mechanical strength, minimal oxygen permeability, quick biological degradability, remain intact."*

In claim 25 the examiner objects to "lower polyfunctional alcohols". It is respectfully submitted that examples of lower polyfunctional alcohols are given in the specification (page 1, last paragraph). Therefore, it is apparent to a person skilled in the art what is meant by this phrase.

Claim 31 has been reworded in view of the examiner's objection.

Reconsideration and withdrawal of the rejections under 35 USC 112 are respectfully requested.

**Claim Rejection under 37 CFR 1.75(c)**

Claim 32 is objected to under 37 CFR 1.75(c) for failing to further limit the subject matter of the previous claim. This rejection is not understood. The examiner argues that claim 25 encompasses a method for producing a polymer blend using steps a) and b) and states that claim 32 encompasses a step of producing a hydrolyzed component. This hydrolyzed component is one of the components used in step a9. Therefore, claim 32 defines how one of the components for producing the polymer is to be prepared. This is a further limitation of the process of producing the polymer blend.

In any case, the limitation of claim 32 has been introduced into claim 25, and claim 32 is canceled.

**Rejection under 35 U.S.C. 102**

Claims 20, 22, 24 stand rejected under 35 U.S.C. 102(b) as being anticipated by *Ritter et al.* (US 5,439,953).

Claim 20 has been amended by including the feature of claim 23 so that the above rejection no longer applies.

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**Rejection under 35 U.S.C. 103**

Claims 20, 22, 24 stand rejected under 35 U.S.C. 103(a) as being obvious in view of *Ritter et al.* (US 5,439,953).

Claim 23 stands rejected under 35 USC 103(a) as being unpatentable over *Ritter et al.* and *Stepto et al.* Claim 23 has been incorporated into claim 20. Therefore, the rejection over *Ritter et al.* and *Stepto et al.* will be addressed in the following.

The examiner argues that the prior art reference discloses a starch-based polymer compound with a starch content of 40 to 50 % and a synthetic polymer content of 25 to 40 %. Ethylene glycol etc. can also be used and is interpreted by the examiner as hydrolysis component. The disclosed polymers include polyvinyl acetate.

Claim 20 defines that the thermoplastic polymer blend comprises a thermoplastic starch, at least one synthetic polymer, a hydrolyzed polyvinyl acetate (PVAc) saponified to a hydrolysis degree of 20 to 70 %, and an acidic catalyst, wherein the starch component of the polymer blend has a molecular weight which is only minimally reduced relative to native starch and wherein the thermoplastic polymer blend has a bi-continuous phase structure.

The patent to *Ritter et al.* discloses starch-based materials and molded parts modified by synthetic polymers. The starch is thermomechanically digested at elevated pressures and temperatures and contains synthetic polymer compounds in at least largely homogenous mixture. These synthetic thermoplastic polymer compound is present as an aqueous polymer dispersion during processing and the thermoplastic polymer has been incorporated in combination with the aqueous phase in such a way that the starch digestion has been effected by the concomitant use of the aqueous phase of the polymer dispersion. The starch digestion preferably is carried out in a one step process while mixing the aqueous polymer dispersion into the starch.

Even though the prior art mentions that polyvinyl acetate can be used as the thermoplastic polymer in the blend, there is no indication or suggestion that the polyvinyl acetate is hydrolyzed to a degree of 20 percent to 70 percent. The components ethylene glycol etc. mentioned in *Ritter et al.* are used as plasticizers in addition to or in place of water. As mentioned in *Ritter et al.* (col. 6, lines 53 to 56), **thermomechanical** starch

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digestion takes place in the extruder. As discussed above, such thermomechanical digestion leads to starches having a significantly reduced molecular weight as evidenced in the table on page 7 of the instant application. The molecular weights resulting from thermomechanical digestion (product TPS) are much lower than the minimally reduced molecular weight achieved according to the present invention (see page 7 of the instant specification).

The examiner cites *Stepito et al.* to show the use of acid catalysts for deconstructing starch. *Stepito et al.* discloses that the molecular weight of the starch is reduced by a factor 2 to 5000 when adding an acidic catalyst. The disclosed use of the acidic catalyst in *Stepito et al.* for the purpose of deconstructing the starch and reducing its molecular weight cannot be viewed as an incentive to employ the chain scission catalyst for the purpose of improving the properties of the blend, including keeping the molecular weight high. The instant specification shows that the addition of an acidic catalyst reduces the molecular weight of the starch more than in the thermomechanical process used for TPS (see examples 1, 2, 3 of page 7). Therefore, a person skilled in the art would not consider the addition of a known acidic chain scission catalyst to a starch mixture when trying to improve the properties of the starch blend.

The blends of the present invention are moreover characterized by a bi-continuous phase structure imparting to the blend the hydrophobic properties of the synthetic polymer component even for a relatively minimal proportion within the total mixture and, at the same time, the properties of the thermoplastic starch, such as high mechanical strength, minimal oxygen permeability, and quick biological degradability (see page 5, lines 11-24). These properties allow the production of films from the blend according to the invention.

The blends of *Ritter et al.* are suitable only for injection molding.

Reconsideration and withdrawal of the rejection of claims 20, 22, 24 under 35 USC 103 over *Ritter et al.* and *Stepito et al.* are respectfully requested.

Claim 21 stands rejected under 35 U.S.C. 103(a) as being unpatentable over *Ritter et al.* and *Sachetto et al.* (EP 0 404 723).

*Sachetto et al.* discloses a composition containing starch, at least one copolymer, and a thermoplastic polymer. Also disclosed are suitable additives.

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As pointed out above, the patent to *Ritter et al.* does not disclose the basic composition as claimed in claim 20. Therefore, the disclosure of additives cannot make obvious the subject matter of claim 21 that depends from claim 20.

Claims 25, 28-31, 36-37 stand rejected under 35 USC 103(a) as being unpatentable over *Ritter et al.* and *Stepito et al.* (US 5,382,611).

Claim 25 has been amended to include the features of claim 32 so that the above rejection no longer applies. However, claims 32-35 and 39 stand rejected under 35 USC 103(a) as being unpatentable over *Ritter et al.*, *Stepito et al.*, and *Sachetto et al.* Therefore this rejection will be addressed in the following.

As pointed out by the examiner, *Ritter et al.* does not mention an acid catalyst.

The examiner cites *Stepito et al.* to show the use of acid catalysts for destructurizing starch. *Stepito et al.* discloses that the molecular weight of the starch is reduced by a factor 2 to 5000.

*Sachetto et al.* disclose the use of PVAc/PVOH in connection with destructurized starch and polymers but not the use of an acidic catalyst in this connection.

In the present invention, the acidic catalyst is used not to destructurize the starch (i.e., reduce the molecular mass) but to improve the properties of the blends, including keeping the molecular weight at a level as high as possible. As pointed out in the instant specification (page 4, lines 19ff), the acidic catalyst, contrary to prejudice in the art, was found to promote the quickly occurring transesterification or cross-linking reaction of starch, of the hydrolyzed PVAc, and synthetic polymer in the presence of water. This improves the molecular weight, rheological properties, and melt viscosity of the blends. The acid-catalyzed reaction occurs in the shearing field of the extruder so that it is possible to carry out processing with relatively large amounts of moisture in the mixture. The addition of the catalyst also allows adjustment of the rheologic properties of the mixture within certain limits so that the adjustment of the viscosity of the blends can be improved. It is possible to adjust excellent reproducible processing conditions within the extruder.

This is not obvious in view of cited prior art references. Even if the *Ritter et al.* composition were changed to include the hydrolyzed PVAc component as suggested by *Sachetto et al.*, it would not be obvious to add an acidic catalyst because *Stepito et al.*

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clearly teach that adding an acidic catalyst will lead to destructured starch that has a greatly reduced molecular weight (up to a factor 5000!) - *Stepito et al.* refer to the acidic catalyst as a chain scission catalyst. The disclosed use of the acidic catalyst in *Stepito et al.* for the purpose of destructuring the starch and reducing its molecular weight cannot be viewed as an incentive to employ the chain scission catalyst for the purpose of improving the properties of the blend, including keeping the molecular weight high.

Therefore, a person skilled in the art would not consider the addition of a known chain scission catalyst to a starch mix when trying to improve the properties of the starch blend.

However, contrary to all expectations, the inventors have discovered that acidic catalyst imparts unexpected properties to the blend. As stated on page 5, lines 1-24, of the instant specification, the rheological properties can be adjusted and the adjustment of the viscosity of the polymers can be improved (see also page 6, lines 13-15; higher melt viscosity). Also, bi-continuous stable phase morphology of the blend results, and this allows the production of transparent films. Hydrophobic properties of the synthetic polymer component is imparted to the blend as a whole; the high mechanical strength, minimal oxygen permeability and quick degradability, properties of the thermoplastic starch are maintained. Molecular weight reduction is observed only to a limited extent (page 6, lines 17-18, of the instant specification). The tensile strength  $\rho_{max}$  as well as the tensile module are increased for the blends of the present invention as evidenced by examples 15 (without acidic catalyst) and 16 (acidic catalyst added). Also, the example 15 and 16 demonstrate that the blend 16 according to the invention enables the production of films that are substantially thinner (reduced from 80-100  $\mu\text{m}$  for example 15 to 60 to 80  $\mu\text{m}$  for example 16) than with prior art blends. See also the Table on page 12 of the instant specification showing various examples where the film thickness is typically 30 to 60  $\mu\text{m}$  for the inventive blends.

Moreover, the PVAc/PVOH components of *Sachetto et al.* are technical products (Airvol 540S; Pebax MA-4011); such technical products have statically distributed OH groups within the PVAc. The present invention uses an aqueous PVAc dispersion that is saponified at 120 to 140 °C (see page 6, lines 2-4, of the instant specification). Such a

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process leads to block-saponified PVAc.

In view of the above arguments, neither claim 25 drawn to a method nor claim 20 drawn to a thermoplastic polymer blend is obvious in view of *Ritter et al.*, *Stepto et al.*, and *Sachetto et al.*

Claims 26-27 stand rejected under 35 USC 103(a) as being unpatentable over *Ritter et al.*, *Stepto et al.*, and *Otey et al.* (US 3,949,145). Claim 38 stands rejected under 35 USC 103(a) as being unpatentable over *Ritter et al.*, *Stepto et al.*, and *Anderson et al.* (US 6,231,970). The claims 27, 27, and 38 are believed to be allowable as dependent claims of claim 25.

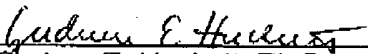
### CONCLUSION

In view of the foregoing, it is submitted that this application is now in condition for allowance and such allowance is respectfully solicited.

Should the Examiner have any further objections or suggestions, the undersigned would appreciate a phone call or e-mail from the examiner to discuss appropriate amendments to place the application into condition for allowance.

Authorization is herewith given to charge any fees or any shortages in any fees required during prosecution of this application and not paid by other means to Patent and Trademark Office deposit account 50-1199.

Respectfully submitted on August 2, 2004,

  
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- Chemical and Petroleum Engineering Department - Formation of ... (2 pages)

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## UNDERGRADUATE

### Formation of Co-Continuous Open-Celled Morphologies in Biopolymers

**Todd Crosby, University of Pittsburgh**  
**Advisor: Professor Sachin Velankar**

The objective, of this project, is to research various methods of forming co-continuous (bi-continuous) morphologies in two component blends. Each phase is interlocked within one another and removal of one phase will leave the other self-supporting. Applications of these structures include biological scaffolds for cell regeneration, electrically conductive polymers, as well as numerous uses in the food industry. One popular method is the non-equilibrium phenomenon, spinodal decomposition. However, this unstable state, coarsens, or forms droplets, and the bi-continuity is lost. One way to 'freeze' the structure is through gelation. Further exploration showed that a co-continuous morphology with one phase removed is open. Another way to form an open-cell structure is by foaming. A problem with this is that cells tend to collapse. This is an open-ended project in its early stages of development.



Searching through literature yielded two interesting options to be examined. One path is to foam a substance that is already gelled. The other route is spinodal decomposition with a biopolymer blend. The system chosen for spinodal decomposition was the easily accessible gelatin/dextran mixture. There is extensive information on this protein/polysaccharide system, such as phase diagrams and gelation under certain controllable conditions. However, there is limited information on the modulus and tensile strength of this system as a function of time and at various quench depths and concentrations. These values will also be a function of porosity size. A useful contribution would be to report this information and test the strength limits of possible scaffolds.

The second path is to start with an aqueous solution of gelatin gel form and foam the substance. This is to be done using a high-pressure cell to dissolve carbon dioxide allowing a certain amount to diffuse into the gel. The pressure is then rapidly dropped so that the CO<sub>2</sub> nucleates and forms an open-celled structure. This is advantageous because there is only one component and it will be in solid-like form. Various moduli and

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stiffness of gels will be tested during the foaming process.

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## JOURNAL OF MACROMOLECULAR SCIENCE\*

Part C—Polymer Reviews

Vol. C43, No. 1, pp. 87–141, 2003

# Formation of Co-continuous Structures in Melt-Mixed Immiscible Polymer Blends

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### ABSTRACT

Co-continuous structures can be regarded as the coexistence of at least two continuous structures within the same volume. Blends with co-continuous structures may combine the properties of both components in a favorable way, for example, mechanical moduli. This review article deals with the identification, characterization, and properties of co-continuous structures as well as with the development of co-continuous structures during the melt blending process.



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### Co-continuous Structures in Polymer Blends

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Co-continuous structures usually can be formed within a composition region about the phase inversion composition, which mainly depends on the viscosity ratio. On the other hand, co-continuous structures can be found independent of composition as intermediate stages during the initial state of morphology development and during phase inversion process in blends in which the component finally forming the dispersed phase forms the matrix in early mixing states. In addition, even at low volume fractions of one component, stable co-continuous morphologies can be created using suitable processing conditions, forming long elongated interconnected structures that do not break up because of the flow. The interfacial tension plays an important role for the stability; a lower interfacial tension leads to broader composition ranges of co-continuous structures. Another factor enhancing the formation and stability of co-continuous structure is melt yield stress of one or both components of blends. In addition, this article reviews the stability of co-continuous structures during further processing and the influence of compatibilization on the structure formation and stability. Subsequently, two models describing the co-continuous composition range are discussed.

**Key Words:** Co-continuous structure; Phase inversion; Polymer blends; Blend morphology.

## 1. INTRODUCTION

Polymer blends have become an important route to new, high-performance polymeric materials over the last 40 years. The technique of blending polymers can serve many different purposes. By using suitable blend technology, combinations of a wide range of physical, mechanical, and other properties can be achieved and adjusted to the needs of particular end-use applications. Often synergistic effects can be achieved.<sup>[1]</sup> Other reasons to use blends can include improved processing behavior or lower cost. Most commercial polymer blends are immiscible because of their high molecular weights and unfavorable interactions and, thus, form multiphase structures.

The properties of multiphase materials are determined by the properties of the component polymers, by the adhesion between phases, and by the blend morphology that is created during the melt mixing process.<sup>[2]</sup> The morphology development depends on the rheological properties of the blend components, interfacial tension, blend composition, and processing conditions.<sup>[3]</sup>

The structure obtained after mixing of immiscible polymer pairs can be categorized into four basic morphology types (Fig. 1):

- Matrix-dispersed particle structures
- Matrix-fiber structures
- Lamellar structures
- Co-continuous structures

Most commercial polymer blends have matrix-dispersed particle structures.<sup>[2]</sup> Especially for rubber toughening of polymers, a great deal of knowledge has been developed concerning the influence of rubber particle size, rubber type, rubber



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content, and interfacial properties on mechanical properties. There is an increasing interest in co-continuous blends because this morphology type can offer some better combinations of the component properties than are possible from dispersed-type structures.<sup>[4,5]</sup> For example, a co-continuous structure gives the maximum contribution to the mechanical modulus from each component simultaneously.<sup>[5,6]</sup> Synergistic effects on impact properties have also been shown in the literature.<sup>[7,9]</sup>

Examples of commercial co-continuous blends include conductive modified PP/PE/EPR-blends,<sup>[10,11]</sup> PP/PU-blends<sup>[12]</sup> or PA6/PPE-blends,<sup>[13,14]</sup> and co-continuous blends based on PA6/ABS<sup>[15-17]</sup> having high impact properties.

To take advantage of co-continuous structures in materials produced by melt mixing, it is important to understand which processing conditions lead to their formation and especially the conditions for their stability. It is still not clear under what conditions and by which mechanism a co-continuous structure may be formed, and whether a co-continuous structure can be stable or if it is simply an unstable intermediate that eventually transforms into a dispersed morphology. Therefore, this paper tries to summarize the state of knowledge about this structure type.

Co-continuous structures can result from a number of different processes. Although we will focus on melt mixed blend systems, co-continuous structures formed during the demixing process of miscible systems by spinodal decomposition are known and well investigated.<sup>[18]</sup> Since most industrially useful polymer combinations with high molecular weights are completely immiscible systems without a miscible region under the melt mixing conditions, this mechanism is more an exception in melt-produced polymer blends. A second way to get co-continuous structures, but on the mixing level of polymer chains, is the synthesis of interpenetrating molecular networks.<sup>[19,20]</sup> This level of mixing cannot be achieved by melt mixing, only by simultaneous or sequential chemical synthesis of the polymers themselves. Block copolymers can form co-continuous structures of the blocks for certain block lengths and compositions.<sup>[21-24]</sup>

## 2. DEFINITION AND DESCRIPTION OF CO-CONTINUOUS STRUCTURES

There are different opinions about how to define co-continuous structures in polymer blends. Two main views are summarized here. The first describes an ideally co-continuous structure in a classic way, which is defined as the coexistence of at least two continuous structures within the same volume; this means both components have three-dimensional spatial continuity on some finite scale of mixing.<sup>[25]</sup> In a co-continuous polymer blend, each component is a polymer phase with its own internal network-like structure from which its properties result. This general definition includes different scales of mixing. In fact, in the literature, co-continuous phase structures are often also described as interpenetrating polymer networks (IPNs), in which the network is formed of macroscopic phase volumes<sup>[25]</sup> and are called thermoplastic IPNs,<sup>[19]</sup> IPNs of phases,<sup>[6]</sup> interpenetrating co-continuous phase structure,<sup>[26]</sup> interpenetrating phase structures (IPs),<sup>[27]</sup> or interpenetrating polymer blends (IPBs).<sup>[28]</sup> The term IPN more typically refers to a bicontinuous structure on the mixing level of polymer chains.<sup>[20]</sup> Other terms used in the literature to describe

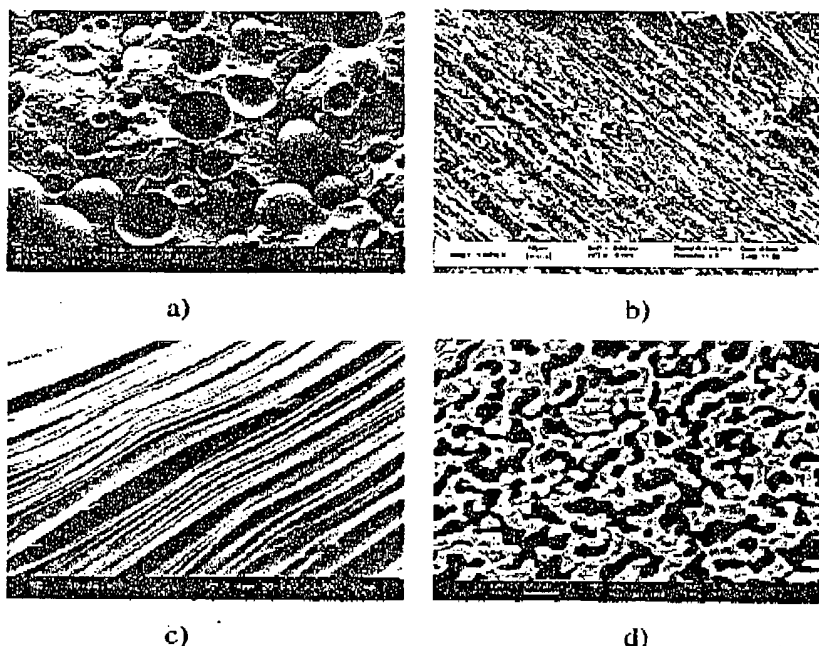


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## Co-continuous Structures in Polymer Blends

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**Figure 1.** Types of morphology in immiscible polymer blends, illustrated by SEM photomicrographs of cryofractures. (a) Dispersed structure (TPU/PP = 80/20 blend); (b) matrix-fiber structure (PA6/SAN = 30/70 blend); (c) lamellar structure (PP/EPDM = 80/20 blend) (Reproduced by permission from Ref.<sup>[157]</sup>); (d) co-continuous structure (PE/PS compatibilized 25/75 blend, PS etched).

co-continuous structures are structures with dual-phase continuity<sup>[26,29-31]</sup> or co-phase continuity.<sup>[32]</sup>

In a binary co-continuous blend, the surface of each phase is an exact, topological replica of the other; they are complementarily reversed (antitropic), as shown in Fig. 2. Co-continuous structures can be formed over a certain interval of volume fractions. The co-continuous range can be very narrow or quite wide and is centered about the phase inversion composition  $\phi_{PI}$ , which is also called the *phase inversion point*. Equations have been developed to estimate this composition, and these are discussed in Sec. 3. A model describing the volume range in which co-continuous structures can be formed is presented in Sec. 6.1.

The second definition is based on the percolation threshold theory and takes into account that the structures formed by melt mixing of polymers represent a coexistence of different structure types rather than an ideal network. Lyngaae-Jørgensen and



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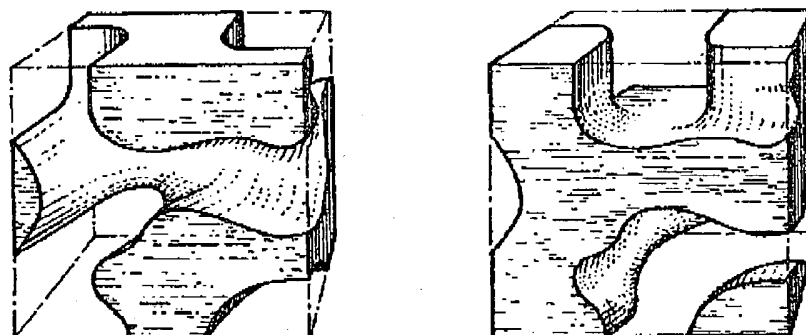


Figure 2. Model of the antitropic structure of both components of a co-continuous blend according to Gergen (Reproduced by permission from Ref.<sup>[25]</sup>).

Utracki<sup>[26,27,31,33]</sup> define a co-continuous structure as one in which at least a part of each phase forms a coherent continuous structure that permeates the whole volume. This definition also allows some part of the components to exist in discrete domains that are not part of the network structure. The volume fraction at which the system changes from containing only discrete domains of one phase to a system containing one infinite structure (and discrete domains) defines the transition point and can be also expressed as the critical volume fraction,  $\phi_{cr}$ , or percolation threshold, as shown in Fig. 3. Significant changes in the properties of the blend occur at this point. As the volume fraction increases, the proportion of the minor component incorporated in the percolation structure increases. At a certain volume fraction, this entire component becomes part of the percolation structure, thereby achieving a fully co-continuous structure. The continuity index  $\Phi_c$ ,<sup>[27]</sup> also called the degree of (co-)continuity,<sup>[26,31,33]</sup> interpenetration index,<sup>[26,31]</sup> or continuity fraction,<sup>[34]</sup> represents the portion of a component that is part of the percolating structure. Its calculation is described in Sec. 4.1.2.

In a certain sense, the first definition is a special case of the second one in the situation when the continuity index is equal to one for both phases. In most papers included in this review, the term "co-continuous structure" is generally used more in the sense of the first definition, which means a complete network structure of both polymers. If not stated otherwise, we will follow this definition. Some authors also use the term "fully co-continuous structure" to distinguish this case from the second definition. The disadvantage of the second definition is that the "continuity index" is required to describe the structure and its influence on properties, but on the other hand, the advantage of this definition is this connection with properties. Some other aspects related to this definition will be discussed in Sec. 6.2.

To develop co-continuous structures by intensive mixing of two molten polymers in a shear field, the most effective mixing can be achieved when the viscosities and the volume fractions of the two components are equal (equivolume,





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## Co-continuous Structures in Polymer Blends

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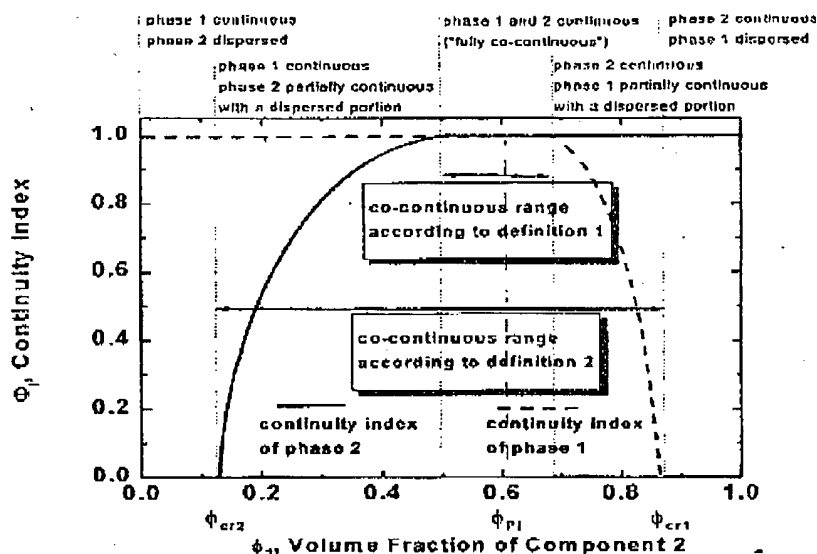


Figure 3. Co-continuous structure composition range using definition 1 and definition 2 [according to Lyngaae-Jørgensen and Utracki<sup>[26,27,33]</sup> using the critical volume fraction  $\phi_{c12}$ , the continuity index  $\phi_{c1}$ , and the phase inversion composition  $\phi_{P1}$ .

equiviscous mixing). Equal-volume fractions maximize the opportunity for maintaining connectivity because neither component is present in a minor amount. But in most systems, the viscosities of the components are different. The low-viscosity phase tends to be continuous because this minimizes energy dissipation in the flow field. To compensate for this tendency, the volume fraction of the higher-viscosity component has to be increased to the same extent as the viscosities differ to maintain the connectivity between the phases. This relation is shown qualitatively in Fig. 4. These considerations are the basis for some of the equations for the phase inversion composition, which are described in Sec. 3.

In a quiescent melt, a co-continuous structure will be transient, in the absence of a kinetic barrier to flow, because the interfacial tension between the incompatible polymer components drives the system toward a minimum surface free energy. This will result in breakup of the co-continuity and lead to phase domain growth. Only when the network structure is kinetically inhibited from breakup and retraction can the co-continuous structure be preserved. This can be achieved by chemical or physical crosslinking of at least one phase or of the interphase. Rapid quenching of such a melt, prior to retraction, will preserve the structure by crystallization or vitrification. In processing, it should be possible to maintain the co-continuous structure by suitable flow conditions which prevent breakup and retraction. Stability of co-continuous



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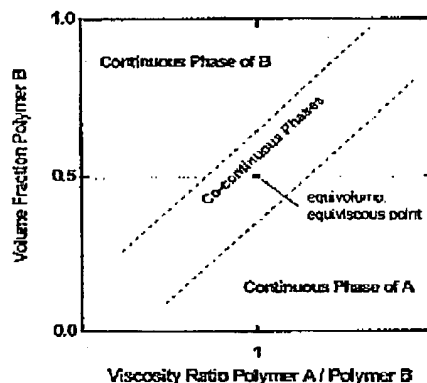


Figure 4. Relation between the volume range of co-continuous structures and the viscosity ratio.

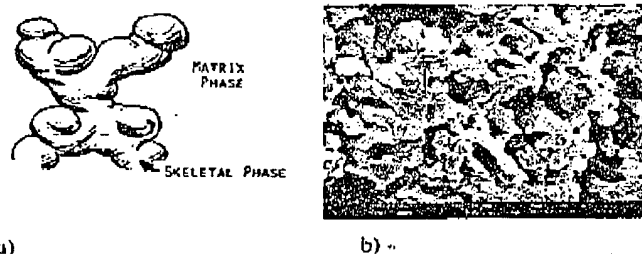


Figure 5. (a) Model of the skeletal structure type according to Gergen (Reproduced by permission from Ref.<sup>[25]</sup>). (b) SEM of a PA6/ABS = 50/50 blend after etching of PA6 showing the skeletal structure type.

structures will be discussed in Sec. 5.3. for noncompatibilized as well as for compatibilized and reactive blends.

It has been shown that structural rearrangement or retraction can be inhibited in blends containing thermoplastic elastomers, like styrene-butadiene-styrene (SBS) copolymers and hydrogenated versions such as styrene-ethylene-butene-styrene (SEBS) copolymers,<sup>[25,35-37]</sup> or poly(ether ester) (PEE) copolymers based on poly(tetramethylene oxide) and poly(butylene terephthalate) segments.<sup>[36,38,39]</sup> In addition, these blends can show very broad co-continuous composition ranges. This effect was first observed and discussed by Gergen,<sup>[25,35]</sup> who indicated that some block copolymers can form a skeletal structure, as illustrated in Fig. 5. Because they are usually the component with the higher surface tension and viscosity,



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the block copolymers form convex surfaces of the skeletal structure. The other polymer takes up the antitropic continuous structure. The factor preventing breakup and retraction is the yield stress, which is typical for these block copolymers in certain compositions, as shown by Gergen,<sup>[35]</sup> Elmendorp,<sup>[40]</sup> and Veenstra.<sup>[38]</sup> Therefore, such blends are very stable over wide processing conditions,<sup>[25,35,36-39,41,42]</sup> which is in contrast to other co-continuous blends. Because of their special behavior, blends with components exhibiting a yield stress will be discussed separately in Sec. 5.4 in detail.

## 3. EQUATIONS FOR THE PHASE INVERSION COMPOSITION

It is the final state of dispersion that is important to the end-use properties of a polymer blend. The component that forms the matrix generally dominates the properties of the blend. Thus, in co-continuous blends, both components contribute more equally to the properties. Because of these morphology-property relations, it is of interest to determine in advance which phase will form the matrix and at which compositions co-continuous structures most likely can be formed. Some attempts have been made over the last 25 years to estimate the phase inversion composition  $\phi_{PI}$  in terms of material properties and processing conditions and to compare these equations with experimental findings. Usually co-continuous structures can be formed within a composition region about  $\phi_{PI}$ . Naturally, the phase inversion compositions reported in the literature, and the range of compositions where co-continuous structures form, depend not only on material and processing parameters but also on the experimental concentration step size used and the identification method employed.

The following is a simple relationship describing the phase inversion composition in terms of volume fractions and viscosities stemming from the considerations presented in Sec. 2 (see Fig. 4).

$$\phi_{1,PI}/\phi_{2,PI} * \eta_2/\eta_1 \cong 1 \quad (1)$$

where  $\eta_i$  is the viscosity and  $\phi_{i,PI}$  is the volume fraction at phase inversion of the component  $i$ . Using  $\lambda = \eta_1/\eta_2$  and  $\phi_{1,PI} = 1 - \phi_{2,PI}$  the phase inversion composition becomes:

$$\phi_{2,PI} = 1/(1 + \lambda) \quad (2)$$

This idea was first suggested from data by Avgeropoulos et al.<sup>[43,44]</sup> in 1976 and was generalized by Paul and Barlow<sup>[45]</sup> in 1980. The relationship was expressed in terms of the equation shown by Jordhamo et al.<sup>[46]</sup> in 1986 and later extended by Miles and Zurek<sup>[23]</sup> in 1988.

For blends without interlayer slip, there is stress continuity across the interface between matrix and dispersed particles. For non-Newtonian fluids, the viscosity ratio should be calculated at the shear stress used for the preparation of the blends.<sup>[5,33,47]</sup> Avgeropoulos<sup>[43,44]</sup> used the torque ratio ( $\tau_1/\tau_2$ ) rather than the viscosity ratio, which is convenient since such blends are often mixed in a torque rheometer or similar compounding devices. In blends with large viscosity differences, the use of viscosity ratios calculated at constant shear rate, as introduced by